This Page Is Inserted by IFW Operations and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.



11) Publication number:

0 435 062 A1

(12)

EUROPEAN PATENT APPLICATION

21) Application number: 90123809.7

2 Date of filing: 11.12.90

(5) Int. Cl.⁵: **C10M** 107/38, C10M 111/04, C10M 169/00, C10M 169/04, //(C10M111/04,107:38,107:38), (C10M169/00,107:38,119:22, 147:00),(C10M169/04,107:38, 147:00),C10N20:04,C10N30:06

Priority: 12.12.89 IT 2267289

Date of publication of application:03.07.91 Bulletin 91/27

Designated Contracting States:
 BE DE ES FR GB IT NL SE

Applicant: AUSIMONT S.p.A. 31, Foro Buonaparte I-20121 Milano(IT)

2 Inventor: Corti, Costante 1, Via Chopin I-20141 Milan(IT) Inventor: Savelli, Paolo 41, Via Vittorio Veneto
I-20091 Bresso-Milan(IT)
Inventor: Montagna, Laura
63, Via Porpora
I-20131 Milan(IT)

Inventor: De Pasquale, Raiph J. 18, Pembroke Drive Mendham, N.J. 07945(US)

(4) Representative: Barz, Peter, Dr. et al Patentanwälte Dipl.-Ing. G. Dannenberg Dr. P. Weinhold, Dr. D. Gudel Dipl.-Ing. S. Schubert, Dr. P. Barz Siegfriedstrasse 8 W-8000 München 40(DE)

Perfluoropolyether lubricants having improved antiwear properties.

Described is the use, as lubricants endowed with improved antiwear properties, of compositions comprising:

(A) from 100 to 0.1% by weight of a polyether of general formula (I):

435 062 /

wherein:

T and T',

the same of different from each other, are inert end groups of formula -CF₂X, -C₂F₄X,

-C₃F₆X or fluorinated reactive end groups containing carboxy and/or hydroxy and/or

ketone and/or amide and/or amine and/or alkoxy groups,

at least one of T and T' being a reactive end group;

X is

m, n, s and p are in

are integers such that the polyether has an average molecular weight of from about 1,000 to about 100,000;

(B) from 0 to 99.9% by weight of certain perfluoropolyethers having non-reactive end groups.

Said lubricating compositions can also be used, in combination with suitable thickening agents, for the formulation of lubricating greases having improved antiwear properties.

PERFLUOROPOLYETHER LUBRICANTS HAVING IMPROVED ANTIWEAR PROPERTIES

The present invention relates to compositions based on perfluoropolyether compounds endowed with lubricating characteristics and improved antiwear properties.

It is known from IT-A-20,322 A/86 to use fluid perfluoropolyethers endowed with a kinematic viscosity of from 8,000 to 40,000 cSt at 20 °C as lubricating oils or components of perfluorinated lubricating greases in order to obtain lubricants having a low friction coefficient.

In said document it is demonstrated that it is not possible to obtain a low friction coefficient when using perfluoropolyethers of the straight-chain type endowed with a low kinematic viscosity, for example 30 to 250 cSt.

On the other hand it has been found that the antiwear properties of a perfluoropolyether cannot be directly correlated to the friction coefficient, i.e., said properties do not improve as the viscosity increases.

Furthermore, from IT-A-20,159 A/86 there are known several additives for lubricants based on perfluoropolyether compounds, which impart antirust properties to said perfluoropolyethers.

Also in that case these additives do not seem to impart particular antiwear properties to the perfluoropolyether lubricants, which shows that said properties also cannot directly be correlated to the antirust properties.

On the other hand, the antiwear characteristics of perfluoropolyether lubricants are similar to those of mineral oils and not fully satisfactory for most of the practical applications of lubricants.

It has now been found that lubricants consisting of fluoropolyethers having the general formula (I):

$$TO(CF2O)m(CF2CF2O)n(CF2CFO)s(CFO)pT' (I)$$

$$CF3 CF3$$

or compositions based on perfluoropolyethers as defined hereinafter, containing the fluoropolyethers of formula (I) as additives, exhibit improved antiwear properties.

In formula (I), the perfluorooxyalkylene units with the subscripts m, n, s and p are distributed at random along the chain.

The subscripts m, n, s and p in general formula (I) are integers such that the corresponding products exhibit an average molecular weight in the range of from about 1,000 to about 100,000, preferably from about 2,000 to about 5,000. When none of said coefficients is zero, the s/p ratio is about 10, the s/n ratio ranges from about 0.5 to about 1.5 and the n/m ratio is about 10. When n is equal to zero, s/p is about 10, while s/m is about 20; when s and p are equal to zero, n/m ranges from about 0.6 to about 2.

Perfluorooxyalkylene units of formula (- CF_2 - CF_2 -CF

The end groups T and T', the same or different from each other, are selected from inert end groups of formulae CF_2X_7 , $C_2F_4X_7$ and $C_3F_6X_7$ and from fluorinated reactive end groups containing carboxy, hydroxy, amide, ketone, amine and/ or alkoxy groups.

Examples of the latter groups are the following ones:

50

20

30

40

5

wherein:

X is

F or Ct:

R₁ and R₂

, the same or different from each other, are H or (preferably C1-C12) alkyl, alkylaryl or aryl radicals, optionally containing substituents such as, for example, -OH and/or halogens (e.g. F, Cl, Br and I), or in combination with the N atom they form a heterocyclic radical, which optionally contains other heteroatoms such as O, S and P;

Α 40

35

45

50

represents a primary, secondary or tertiary amine or a heterocyclic (nitrogen-containing)

base, optionally containing also other heteroatoms such as O, S and P;

-OCH3, -NH2 or -NR1R2.

At least one of T and T' is a reactive group, e.g., selected from the ones depicted above. In case the subscripts s and p are zero, T and T' are usually selected from

-CF2-CH2OH, -CF2-COOH and -CF2-CN.

The products of general formula (I) are obtainable from the precursors of general formula (II):

wherein m, n, s and p are as defined hereinbefore, while L and L', the same or different from each other, may be selected from inert end groups of formulae -CXF2, -C2XF4 and -C3XF6 (X = F, CI) and from reactive end groups of the following formulae

$$-\mathrm{CF}_2\mathrm{-COF}, \quad -\mathrm{CF}_2\mathrm{-C} = 0, \quad -\mathrm{CF}_2\mathrm{-CF}_2\mathrm{-COF}, \quad -\mathrm{CF}_2\mathrm{ocoF},$$

$$\begin{vmatrix} & & & & & \\ & & & \\ & & & & \\ & & &$$

10 at least one of L and L' being one of said reactive end groups.

In the compounds of formula (II), groups of formulae (-CF₂CF₂CF₂O-) and/or (-CF₂CF₂CF₂O-) may also be present.

The precursors of formula (II) are preparable, according to known techniques, by reaction of one or more perhaloolefins, such as, e.g., tetrafluoroethylene, hexafluoropropene and chlorotrifluoroethylene with oxygen in the presence of ultra-violet radiation, at temperatures of from -80 °C to +40 °C, in the presence or absence of solvents, and by subsequent heat-treatment, at 200 to 250 °C, of the products so obtained in order to decompose the peroxide groups (-O-O-), if any, present therein.

In the compounds of formula (II), X is F when n is zero, while when s and p are equal to zero, the reactive end groups usually are -CF2COF and X is F or CI.

The products of formula (I) can be obtained from those of formula (II) either directly or by reaction of the reactive end groups present in the latter with suitable reagents, such as H_2O or amines of formula NHR_1R_2 , or by further conversion of the resulting groups to yield alcoholic groups by reduction of the corresponding carboxylic groups; nitrile groups by dehydration of the corresponding primary amide groups; and quaternary ammonium carboxylate groups by treatment of the carboxylic groups with amines.

The above compounds of formula (I) can be used not only as such but also as additives which improve the antiwear properties of perfluoropolyethers belonging to one of the following classes:

1.

5

20

25

30

35

40

45

wherein X is -F or -CF₃; A and A', the same or different from each other, are selected from -CF₃, C_2F_5 and C_3F_7 ; the units in brackets are randomly distributed along the perfluoropolyether chain, m and n are integers such that the m/n ratio ranges from about 20 to about 1,000 and the perfluoropolyether viscosity ranges from about 10 to about 4,000 cSt. These perfluoropolyethers may be obtained, e.g., by photo-oxidation of hexafluoropropene according to the process described in GB-A-1,104,482, and by successive conversion of the end groups into inert groups according to the process described in GB-A-1,226,566.

2.

wherein B is $-C_2F_5$ or $-C_3F_7$ and m is an integer such that the product viscosity ranges from about 10 to about 4,000 cSt.

Said compounds may, for instance, be prepared by ionic oligomerization of hexafluoropropene epoxide and successive treatment of the resulting acyl fluoride (COF) with fluorine according to the process described in US-A-2,242,218.

3.

wherein m is an integer such that the product viscosity ranges from about 10 to about 4,000 cSt. These products may, for instance, be obtained by ionic telomerization of hexafluoropropene epoxide and successive photochemical dimerization of the resulting acyl fluoride, according to the process described in US-A-3,214,478.

4. A'O[CF₂CF(CF₃)O]_m(C₂F₄O)_{nt}CFXO)_qA wherein A and A', the same or different from each other, are selected from -CF₃, -c₂F₅ and -C₃F₇; X is -F or -CF₃; m, n and q are integers and can also be equal to 0, but in any case are such that the perfluoropolyether viscosity ranges from about 10 to about 4,000 cSt. These products may be obtained, e.g., by photo-oxidation of mixtures of C_3F_6 and C_2F_4 and successive treatment with fluorine according to the process described in US-A-3,665,041.

5. $CF_3O(C_2F_4O)_p(CF_2O)_qCF_3$ wherein p and q are integers, the same or different from each other, the p/q ratio ranging from about 0.1 to about 5 and, moreover, being such that the product viscosity is from about 10 to about 4,000 cSt. These perfluoropolyethers may be prepared, e.g., by photochemical oxidation of C_2F_4 according to US-A-3,715,378 and subsequent treatment of the photo-oxidation product with fluorine according to US-A-3,665,041.

6. AO-(CF₂-CF₂O)_m-A' wherein A and A', the same or different from each other, represent -C₂F₅ or -C₃F₇, and m is an integer such that the product viscosity ranges from about 10 to about 4,000 cSt. These products may be obtained according to the process described in EP-A-148,482.

7. DO-(CF₂-CF₂O)_rD' wherein D and D', the same or different from each other, are -CF₃ or -C₂F₅, and r is an integer such that the product viscosity is from about 10 to about 4,000 cSt. These products may be prepared according to the process of US-A-4,523,039.

$$R'_{f} = \begin{pmatrix} CF_{3} & R_{f} & R_{f} \\ & C & C & C \\ & CF_{3} & R_{f} & R_{f} \end{pmatrix} R'_{1}$$

wherein R'_f is a perfluoroalkyl group, n is at least 8 and R_f is F or a perfluoroalkyl group.

Preferred perfluoroalkyl groups have from 1 to 8, particularly 1 to 3 carbon atoms. These perfluoropolyethers are described in WO-A-87/00538.

Examples of other basic fluids which can be added to the compounds of formula (I) are, besides those described hereinbefore, paraffinic and/or aromatic mineral oils, polyolefins, siliconic and fluorosiliconic fluids, as well as polyphosphazenes.

The perfluoropolyethers of classes 1 to 8 above have inert perfluoroalkyl end groups, are liquids with a very low vapor tension and exhibit a viscosity, at 20°C, generally ranging from about 50 to about 100,000 cSt, preferably from about 100 to about 2,000 cSt. The compounds of formula (I) are soluble in these fluids.

Thus, another subject-matter of the present invention is the use, as antiwear lubricants, of compositions comprising from 100 to 0.1%, preferably from 10 to 0.5% by weight of a polyether of general formula (I) above, and from 0 to 99.9%, preferably from 90 to 99.5% by weight of a perfluoropolyether (basic fluid) belonging to at least one of classes 1 to 8 given hereinbefore.

The following non-limitative examples are to illustrate the present invention.

Said examples refer to the characterization of lubricating oils comprising perfluoropolyethers of the above classes 1 to 8 and/or fluoropolyethers of general formula (I).

The lubricating oils of said examples, consisting of, or containing or not containing the perfluoropolyethers of said formula (I), have been characterized, as regards their antiwear properties, by means of the four ball wear machine, ASTM D 4172B method, under operative conditions which result in a mixed

5

10

15

20

25

30

35

40

lubrication.

Summary of the utilized measurement method

Three steel balls (0.5 inch in diameter) were fixed inside a suitable container and coated with the lubricant to be evaluated.

A fourth ball of the same type as the preceding ones and placed above them so as to have three contact points, was rotated, under a predetermined load, for a predetermined time. The lubricant was thermoregulated at a given temperature.

The performance of the lubricants was compared on the basis of the average wear diameter of the fixed balls.

Apparatus

10

The test apparatus comprised an electric motor and a pulley system which allowed operation at different speeds of rotation. A spindle, which contained the upper test-piece consisting of a steel ball (0.5 inch in diameter) was integrally connected to the driven shaft.

In a container placed in the proximity of the rotating ball there were arranged three further balls identical, as to diameter and material, with the preceding ball, and fixed and immersed in the lubricant.

The variable load, applied from the bottom upward, pushed the underlying balls against the ball integral with the spindle.

The load was applied by means of a level system.

An induction heating device kept the lubricant temperature inside the container constant; a thermocouple was arranged therein.

Once the predetermined lubricant temperature had been reached, the predetermined load had been applied and the shaft speed of rotation had been selected, the test was started and continued for the predetermined time.

Test conditions

30

20

The reported results refer to tests carried out under the following conditions:

	load	40 kg
35	temperature	75°C
•	speed of rotation	1200 r.p.m.
	time	60 minutes.

40

Preparation of the balls

The balls, of the chrome steel type, made of AISI steel Standard No. E-52100, having a diameter of 0.5 inch, grade 25 EP (Extra Polish), were cleaned and degreased by immersing them first in n-hexane (15 minutes) and then in Delifrene ® HP (trichlorotrifluoroethane) (15 minutes), whereafter they were dried with anhydrous air.

Wear evaluation

Upon completion of the test and without removing the three fixed (lower) balls from the housing, the wear was measured for each ball by means of a microscope having a resolution of 0.01 mm. For each ball, after having removed the oil from the housing by allowing it to drop for 15 minutes and having washed in particular the wear area with Delifrene ® HP, two diameters of the wear impression produced on the surface due to the rotation were measured, one diameter in the direction of rotation and the other diameter perpendicular to the former (6 measurements); then the values were averaged, thereby obtaining the result of the test, which is the average wear diameter (mm).

Examples 1 to 5

Compositions were prepared by using, as basic fluids, perfluoropolyethers having different viscosities, belonging to class 1, of formula:

$$A'O \left(CF_2 - CFO \right)_{m} (CFXO)_{n}A$$

wherein:

5

10

15

20

25

30

35

$$X = CF_3, F;$$
 $A, A' = CF_3, C_2F_5, C_3F_7;$
 $m/n = 20;$

and, as additives, fluoropolyethers having different average molecular weights, of formula:

$$CF_3O(CF_2O)_m(CF_2CFO)_s(CFO)_p^T$$
,
 CF_3
 CF_3

wherein

T =
$$CF_2 - C \frac{OH}{CF_3} (75\%);$$
 $CF_2 - COOH (25\%)$

$$s/p = 10;$$
 $s/m = 20;$ $p/m = 2.$

Said compositions were prepared by mixing the basic fluids with the additives.

The characteristics of each basic fluid and of the additive, their amounts in the composition and the value of the average wear diameter relating to each composition are reported in table 1.

			TABLE 1			
40		BASIC FLUID		ADDITIVE		RESULT
	EXAMPLES	Viscosity at	% by	M-W-	% by.	average wear :
45		20°C (cSt)	wg.		wg.	diameter (mm)
	1	250	95	2400	5	0.50
50	2	250	95	2100	5	0,57
	3	250	90-	2400	10	0.64
55	4	450	97	4150	3	0,60
	5	1200	95	4150	5	0,60

Example 6

The determination of the antiwear properties was carried out only on the additive of example 1, not mixed with any basic fluid.

The average wear diameter was 0.65 mm.

Example 7

5

10

Example 1 was repeated, but using, as additive, the compound of formula:

 $CF_3O(CF_2O)_m(CF_2CFO)_s(CFO)_pT$, CF_3 CF_3 CF_3 CF_3 CF_3 CF_3 CF_3 CF_4 CF_5 CF_5 CF_6 CF_6

having an average molecular weight of about 2,400, in an amount of 6% by weight referred to the mixture with the basic fluid. The average wear diameter was 0.48 mm.

Examples 8 and 9

There were determined the antiwear properties of compositions consisting of the basic fluid of class 1 and an additive of formula:

The characteristics of the compositions and the results of the wear tests are reported in table 2.

50

TABLE 2

1		BASIC FLUI	D	ADDITIVE		RESULT
5	EX.	Viscosity at	% by	Average mol-	% by	Average wear
		20°C (cSt)	wg.	ecular wg.	wg.	dia. (mm)
10	8	250	95	2,400	5	0.50
	9	450	97	2,400	3	0.56

Examples 10 to 12 (comparative)

There were evaluated the antiwear properties of the perfluoropolyethers of class 1, used as basic fluids in examples 3, 4 and 5, without additives. The obtained average wear diameters were 0.85, 0.78 and 0.73 mm, respectively.

Examples 13 and 14

There were determined the antiwear properties of compositions consisting of basic fluids of classes 4 and 5, respectively, having the general formula:

$$A'O \begin{pmatrix} CF_2-CF_0 \\ CF_3 \end{pmatrix}_m \begin{pmatrix} CF_2-CF_2O \end{pmatrix}_n (CFXO)_q A$$

35 wherein:

30

15

$$X = F$$
, CF_3 ;
 $m/n = 1.5$; $m/q = 15$;
 A,A' the same of different from each other, are $-CF_3$
and/or $-C_2F_5$ and/or $-C_3F_7$;

and having a kinematic viscosity at 20°C of 250 cSt and an average molecular weight of about 4,000; and of compound of formula CF₃O(CF₂CF₂O)_p(CF₂O)_qCF₃ wherein p/q = 1;

having a kinematic viscosity at 20°C of 150 cSt and an average molecular weight of about 7,850; or of 5% by weight of the additive of example 1.

The wear tests on the two compositions revealed values of the average wear diameter of 0.53 and 0.70 mm, respectively.

Example 15

There were determined the antiwear properties of a composition consisting of 95% by weight of the perfluoropolyether (basic fluid) of example 14, and of 5% by weight of an additive mixture having a kinematic viscosity at 20°C equal to 80 cSt, consisting of 97% by weight of the compound of formula:

HOCH2-CF2-Rf-CF2-CH2OH

and of 3% by weight of the compound of formula:

HOOC-CF₂-Rf-CF₂-COOH wherein:

Rf = a perfluoropolyether chain having an average molecular weight of about 2,000 and the structure

wherein n/m is 0.7.

The average wear diameter was 0.64 mm.

Examples 16 and 17 (comparative)

The antiwear properties of the perfluoropolyethers used as basic fluids in examples 13 and 14 (classes 4 and 5, respectively), without addition of additives, were evaluated. The average wear diameter was 0.90 and 0.92 m, respectively.

eo Examples 18 and 19 (comparative)

In these two examples there were determined the antiwear properties of a perfluoropolyether of class 5, having a kinematic viscosity, at 20°C, of 250 cSt, admixed with 2% by weight of fluorinated phosphine of formula:

25

30

10

15

 $\begin{bmatrix} c_{3}F_{7}OCF-CF_{2}O-CF-CF_{2} & F \\ CF_{3} & CF_{3} & F \end{bmatrix}_{3}^{P}$

35

(a conventional stabilizer for perfluoropolyethers), and the antiwear characteristics of the same perfluoropolyether, but without additive.

The first test provided an average wear diameter of 1.52 mm and the second test provided an average wear diameter of 0.94

Example 20 (comparative)

A composition was prepared which comprised 97% by weight of a basic fluid consisting of the perfluoropolyether of example 1 and 3% of an additive mixture composed of 97% by weight of a compound of formula:

NC-CF2-Rf-CF2-CN

and 3% by weight of a compound of formula:

HOOC-CF2-Rf-CF2-COOH

wherein Rf is a perfluoropolyether chain having an average molecular weight of about 2,000, and showing the structure depicted in example 15.

Said additive mixture is described in IT-A-20,183 A/88 as a mixture capable of imparting antirust properties to the perfluoropolyether of the present example.

The resulting average wear diameter was 1.04 mm.

55

Example 21

043506241

Example 1 was repeated using, as additive, the compound of formula:

$$\begin{array}{c} \operatorname{CF_3O(CF_2O)_m} \left(\operatorname{CF_2-cFO} \right)_{cf_3} & \left(\operatorname{CFO} \right)_{p} \\ \end{array}$$

wherein s/p = 10; s/m = 20; p/m = 2;

 $T = CF_2 - COOH;$

5

15

20

25

30

40

50

which showed an average molecular weight of about 5,000. The amount employed was 2% by weight, referred to the mixture with the basic fluid. The average wear diameter was 0.69 mm.

Example 22

There were evaluated the antiwear properties of compositions comprising the basic fluid of example 1, using, as additive, the compound of formula:

wherein s/p = 10; s/m = 20; p/m = 2; /OH

which had an average molecular weight of about 2,100.

Compositions containing 2% and 4% by weight of the additive based on the mixture with the basic fluid, were evaluated; the average wear diameter was 0.49 mm for both of said additive concentrations.

Example 23

There were determined the antiwear properties of a grease prepared according to IT-A-1,151,732, containing, as basic fluid, the perfluoropolyether of class 1 described in examples 1 to 5 and having a kinematic viscosity of 1,500 cSt at 20 °C (66.5% by weight), as additive, the additive described in examples 1 to 5 and having an average molecular weight of about 2,250 (3.5% by weight) and, as thickening agent, polytetrafluoroethylene (PTFE) (Algoflon® L 206, produced by the applicant; 30% by weight). The average wear diameter was equal to 0.98 mm.

Example 24

In analogy to example 23, a grease was prepared by using, as basic fluid, only the additive used in example 23 (70% by weight) and, as thickening agent, PTFE (Algoflon® L 206; 30% by weight).

On the grease, the antiwear properties and the average wear diameter, which was equal to 0.70 mm, were determined.

55 Example 25

In analogy to example 23, a grease containing, as basic fluid, the perfluoropolyether used in example 23 (67.8%) and, as additive, the additive (2.2% by weight) described in example 15 was prepared. As thickener

for the formulation of the grease, PTFE (Algoflon® L 206) was used.

From the wear test carried out on the grease so prepared, a value of the average diameter of 0.96 mm was obtained.

Example 26 (comparative)

There were determined the antiwear properties of a grease prepared as described in example 23, containing, as basic fluid, the perfluoropolyether of example 23 and, as thickener, PTFE (Algoflon® L 206).

The average wear diameter was 1.4 mm.

Claims

10

15

20

25

30

35

40

45

50

55

0425062** 1

Use, as antiwear lubricants, of compositions comprising:

(A) from 100 to 0.1% by weight of at least one polyether of general formula (I):

$$\mathsf{TO}(\mathsf{CF}_2\mathsf{O})_{\mathsf{m}}(\mathsf{CF}_2\mathsf{CF}_2\mathsf{O})_{\mathsf{n}} \left(\mathsf{CF}_2\mathsf{CF}_0\right)_{\mathsf{CF}_3} \left(\mathsf{CF}_0\right)_{\mathsf{p}} \left(\mathsf{C$$

wherein:

T and T'. the same or different from each other, are selected from inert end groups of

formulae -CF2X, -C2F4X and -C3F6X and fluorinated reactive end groups containing carboxy and/or hydroxy and/or ketone and/or amide and/or amine

and/or alkoxy groups, provided that at least one of T and T' is a reactive end group;

x is F or Cl;

m, n, s and p are integers such that the polyether has an average molecular weight of from

about 1,000 to about 100,000, provided that when none of said subscripts is zero, s/p is about 10, s/n ranges from about 0.5 to about 1.5 and n/m is about 10, while when n equals zero, s/p is about 10 and s/m is about 20, and when s and p are equal to zero, n/m ranges from about 0.6 to about 2;

units of formula (CF2CF2CF2O) and/or (CF2CF2CF2CF2O) being optionally present in said polyethers;

(B) from 0 to 99.9% by weight of at least one perfluoropolyether selected from at least one of the

following classes 1 to 8; 1.

wherein X is -F or -CF3; A and A', the same or different from each other, are selected from CF3, C₂F₅ and C₃F₇; the units in brackets are randomly distributed along the perfluoropolyether chain, m and n are integers such that the m/n ratio ranges from about 20 to about 1,000 and the perfluoropolyether viscosity ranges from about 10 to about 4,000 cSt;

wherein B is -C₂F₅ or -C₃F₇ and m is an integer such that the product viscosity ranges from about

10 to about 4,000 cSt; 3.

5

10

15

20

25

wherein m is an integer such that the product viscosity ranges from about 10 to about 4,000 cSt; 4. A'O[CF₂CF(CF₃)O]_m(C₂F₄O)_n(CFXO)_qA

wherein A and A', the same or different from each other, are selected from -CF₃, -C₂F₅ and -C₃F₇; X

-CF₃; m, n and q are integers and can also be equal to 0, but in any case are such that the perfluoropolyether viscosity ranges from about 10 to about 4,000 cSt;

5. CF3O(C2F4O)p(CF2O)qCF3

wherein p and q are integers, the same or different from each other, the p/q ratio ranging from about 0.1 to about 5 and, moreover, being such that the product viscosity is from about 10 to about 4,000 cSt;

6. AO-(CF2-CF2-CF2O)m-A'

wherein A and A', the same or different from each other, represent $-C_2F_5$ or $-C_3F_7$, and m is an integer such that the product viscosity ranges from about 10 to about 4,000 cSt;

7. DO-(CF2-CF2O),D'

wherein D and D', the same or different from each other, are $-CF_3$ or $-C_2F_5$, and r is an integer such that the product viscosity is from about 10 to about 4,000 cSt; 8.

30

$$R'_{f} = \left(\begin{array}{c} CF_{3} & R_{f} & R_{f} \\ C & 0 & C & C \\ C & C & C \\ CF_{3} & R_{f} & R_{f} \end{array}\right)_{n} R'_{f}$$

40

35

wherein R'_{t} is a perfluoroalkyl group, n is at least 8 and R_{t} is F or a perfluoroalkyl group.

 Use according to claim 1, wherein the compositions comprise polyether (A) of general formula (I) in amounts of from 0.5 to 10% by weight, and perfluoropolyether (B) in amounts of from 99.5 to 90% by weight.

45

- 3. Use according to any one of claims 1 and 2, wherein the polyether of general formula (I) has an average molecular weight of from about 2,000 to about 5,000.
- Use, as antiwear lubricants, of greases comprising a composition as defined in any one of claims 1 to 3
 and a thickening agent.
 - 5. Use according to claim 4, wherein the thickening agent comprises polytetrafluoroethylene.

EUROPEAN SEARCH REPORT

Application Number

EP 90 12 3809

X A X	EP-A-0 337 425 (AUSIMONT) Page 2, lines 1,2; page 2, line 4 US-A-4 085 137 (R.A. MITSCH) Column 4, lines 10-27; column LU-A-8 146 0 (MONTEDISON) Page 1, line 30 - page 5, line 5 EP-A-0 322 916 (AUSIMONT) Page 4, lines 47-50; page 16, li	7 - page 5, line 3 * - 11, lines 43-47 * - 1	1-5 1,3	C 10 M 107/38 C 10 M 111/04 C 10 M 169/00 C 10 M 169/04 // (C 10 M 111/04 C 10 M 107:38 C 10 M 107:38)
X A X	* Page 2, lines 1,2; page 2, line 4 US-A-4 085 137 (R.A. MITSCH) * Column 4, lines 10-27; column LU-A-8 146 0 (MONTEDISON) * Page 1, line 30 - page 5, line 5 EP-A-0 322 916 (AUSIMONT)	7 - page 5, line 3 * - 11, lines 43-47 * - 1	1,3	M 107/38 C 10 M 111/04 C 10 M 169/00 C 10 M 169/04 // (C 10 M 111/04 C 10 M 107:38
X A X	US-A-4 085 137 (R.A. MITSCH) Column 4, lines 10-27; column LU-A-8 146 0 (MONTEDISON) Page 1, line 30 - page 5, line 5 EP-A-0 322 916 (AUSIMONT)	11, lines 43-47 *	ŧ	C 10 M 111/04 C 10 M 169/00 C 10 M 169/04 // (C 10 M 111/04 C 10 M 107:38
A X	* Column 4, lines 10-27; column LU-A-8 146 0 (MONTEDISON) * Page 1, line 30 - page 5, line 5 EP-A-0 322 916 (AUSIMONT)	11, lines 43-47 1 - 1	ŧ	C 10 M 169/00 C 10 M 169/04 // (C 10 M 111/04 C 10 M 107:38
A X	* Column 4, lines 10-27; column LU-A-8 146 0 (MONTEDISON) * Page 1, line 30 - page 5, line 5 EP-A-0 322 916 (AUSIMONT)	11, lines 43-47 1 - 1	ŧ	C 10 M 169/04 // (C 10 M 111/04 C 10 M 107:38
A X	LU-A-8 146 0 (MONTEDISON) * Page 1, line 30 - page 5, line 5 EP-A-0 322 916 (AUSIMONT)	- -	,3	(C 10 M 111/04 C 10 M 107:38
x	* Page 1, line 30 - page 5, line 5 EP-A-0 322 916 (AUSIMONT)	· -	,3	C 10 M 107:38
x	* Page 1, line 30 - page 5, line 5 EP-A-0 322 916 (AUSIMONT)	· -	,3	
×	 EP-A-0 322 916 (AUSIMONT)	- '		C 10 M 107:38 \
		-	1	
		1		(C 10
	* Page 4, lines 47-50; page 16, li	, ·	,3-5	M 169/00
		nes 1-5; claims 8,9 *		C 10 M 107:38
- 1		-		C 10 M 119:22
P,A	EP-A-0 382 224 (AUSIMONT)	1	-5	C 10 M 147:00)
	* Page 4, line 9 - page 5, line 14;	page 6, example 1 *		(C 10 M 169/04
	— — ·	_		C 10 M 107:38
x	EP-A-0 165 649 (MONTEDISOI	() I 1	-5	C 10 M 147:00)
	laims 1,2; page 17, lines 6-14; page 24, example		_	C 10
	·	-		N 20:04
D,A	EP-A-0 244 838 (AUSIMONT)			C 10 N 30:06
J,/\				
		ļ		
				TECHNICAL FIELDS SEARCHED (Int. CL5)
			,	
ı		ľ		C 10 M
1		.		
1				-
1		Į.		
		1		
1				
1		!		
		1		
		· •		
			Ì	
- 1				
	The present search report has been di	awn up for all claims		
	Place of search	Date of completion of search		Examiner
	The Hague	11 March 91	1	HILGENGA K.J.

CATEGORY OF CITED DOCUMENTS

- X: particularly relevant if taken alone
 Y: particularly relevant if combined with another
- document of the same catagory
 A: technological background
 O: non-written disclosure
 P: intermediate document
- T: theory or principle underlying the invention

- earlier patent document, but published on, or after the filing date
 coument cited in the application
- L: document cited for other reasons
- &: member of the same patent family, corresponding document